

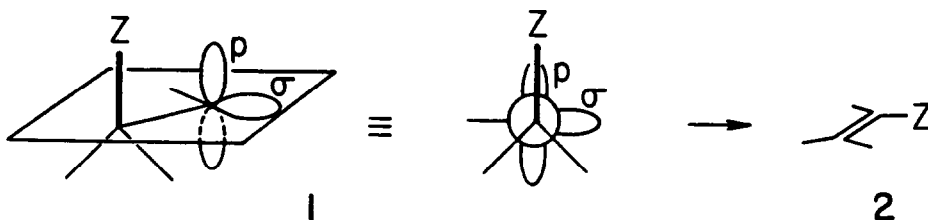
SOLVOLYSIS OF 5-BREXYL BROSYLATES: RELEVANCE TO CARBENE AND CARBOCATION CHEMISTRY

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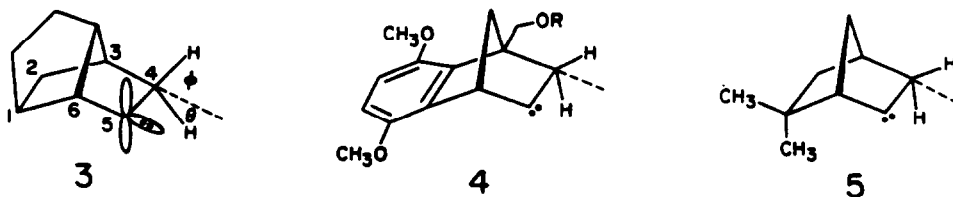
Abstract: Buffered acetolysis of exo- and endo-5-brexyl p-bromobenzenesulfonate and equilibration of the acetates revealed ionic behavior uncharacteristic of norbornyl-type structures. The findings are pertinent to a controversy about carbene rearrangements in 5-brexylidene.

For 1,2-migration in a thermally generated, singlet carbene (1 + 2), it has been proposed on the basis of experiment and supported theoretically that the favored transition state has the C-Z bond aligned with the vacant p orbital.^{1,2} Accordingly, researchers use this geometric model to discuss and interpret various aspects of carbenic behavior.^{1,3}



The experimental basis for this view rests primarily on the rearrangement of 5-brexylidene (3) to 4-brexene.⁴ Deuterium labeling disclosed that exo-H shifted faster than endo-H by a factor of 138.⁵ In the rigid framework of 3, an exo bond at C-4 is better aligned with the carbenic p orbital than is an endo bond;⁶ so the exo preference was taken as evidence that geometry is important in carbene rearrangements.⁴

Subsequently, teams headed by Kyba⁷ and by Freeman⁸ examined 2-norbornyl carbenes such as 4 and 5. In these substrates, the two competing H's are thought to have equal dihedral angles and, in terms of orbital alignment, should be equally inclined to migrate. Their findings showed



however, that exo was favored by factors of 13-20. By analogy to known peculiarities of bicyclo[2.2.1]heptyl cations, they surmised that exo preferences are inherent to norbornyl skeletons. For example, vicinal hydride shifts in norbornyl cations can favor exo migration over endo by factors >100 despite seemingly equal torsional angle relationships.⁹ Also, in solvolysis of exo-norbornyl brosylate, a 3-exo deuterium is known to exert a markedly higher secondary isotope effect than does a 3-endo-d.¹⁰ In cation chemistry, researchers disagree on what factors contribute to such exo-H vs. endo-H differences.¹¹ But whatever they are, Kyba felt that similar factors could operate in carbenes and that conclusions drawn from a norbornyl analog such as 5-brexylidene are on tenuous grounds.¹²

To address this issue, we investigated the acetolysis of exo- and endo-5-brexyl brosylate (6) to determine how closely these analogs mimic typical norbornyl cation behavior. The table summarizes the kinetic and product studies and, for norbornyl brosylates, also includes our rate constants and known product data.¹³ Features of immediate interest are as follows.

Exo- and endo-5-brexyl OBs solvolyze at very nearly the same rate (exo/endo ratio ~ 1.1). (Contrast norbornyl where exo/endo = 1550¹³). The major acetate in each case is that from inversion of configuration. (Contrast norbornyl where the acetate is exclusively exo from either epimeric brosylate.)

To test for thermodynamic stability as a possible controlling influence, we equilibrated the 5-brexyl acetates with HClO₄/HOAc at 25°C.¹⁴ The exo/endo equilibrium constant, approached from both directions, is 1.96, which does not correspond to either of the observed acetate ratios. Importantly, these equilibrations produced no other products, so the 5-brexyl cation has no inclination for vicinal H shifts even under prolonged acidic treatment.

Acetolysis in HOAc/KOAc (5×10^{-3} M) at 25°C^a

Brosylate	Rate		Products (rel%) ^b		K equil exo/endo acetates	Ketone IR (CCl ₄)
	$k \times 10^5 \text{ sec}^{-1}$	k_{rel}	exo acetate	endo acetate		
exo-5-brexyl	1.09 ^{c,d}	39	25	75	1.96	1749 cm ⁻¹
endo-5-brexyl	1.00 ^{c,d}	38	90.3	9.7		
exo-norbornyl	42.8 ^e	1550	99.7	0.3	6.1 ^f	1751 cm ⁻¹
endo-norbornyl	0.0277 ^c	1	99.7 ^g	0.3		

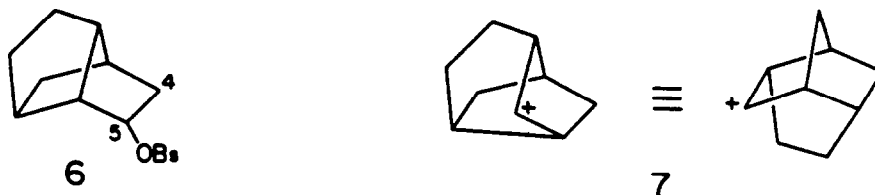
^aMeasured spectrophotometrically (ref. 10). For characterization of all 5-brexyl compounds, see ref. 6. ^bAcetates comprised 94-99% of the products; hydrocarbons are minor components. ^cComputed from rates we obtained at higher temperatures. ^dFor exo-5: ΔH^\ddagger 22.9 kcal/mole, ΔS^\ddagger -4.7 cal/deg mol; for endo-5 the respective values are 23.5 and -2.8. ^eComputed from our k and the known internal return factor of 4.6 (ref. 13). ^fRef. 14. ^gAbout 7% arises by direct displacement (ref. 13).

The predominant inversion from each tricyclic brosylate indicates that nucleophilic capture is not dictated by σ -bridging or by simple steric access in a "limiting" ionization process. Instead, backside solvent intervention wins out; and this aspect also runs contrary to that of norbornyl arenesulfonates.¹⁵

Clearly, in heterolysis, the 5-brexyl system does not manifest any "norbornyl" idiosyncracies; so a basis no longer exists for presuming that the carbenic behavior of 5-brexylidene would do so. The original⁴ conclusions about bond alignment in carbene rearrangements, therefore, remain valid.¹⁶

Our data are pertinent to carbocation chemistry in their own right. An exo/endo acetolysis ratio near unity in conjunction with predominant inversion stereochemistry for each epimer is a very unusual outcome, and appears virtually unprecedented for secondary norbornyl-like structures.^{9c,d} In the norbornyl cation, the reasons for exclusive exo capture are still not agreed upon;^{11,17} but in any case those reasons do not exert control in 5-brexyl solvolysis. Differential angle strain at the cationic site is ruled out as an important influence by the closely similar carbonyl frequencies of 5-brexanone and 2-norbornanone (Table).

It would be tempting to attribute the "non-norbornyl" character of 5-brexyl acetolysis to absence of significant σ -delocalization (because such bridging is akin geometrically to the change 6 \rightarrow 7 and would increase the skeletal strain¹⁸). However, the actual rate constants reveal that whereas exo-5-brexyl OBs solvolyzes slower than exo-norbornyl by a factor of ca. 40,



endo-5-brexyl OBs solvolyzes *faster* than endo-norbornyl by a factor of 38. Therefore, in 5-brexyl, the net exo/endo ratio of ~ 1.1 is due as much to an enhancement of the endo as it is to a slowing of the exo, all relative to norbornyl. In this tricyclic system, nonbonded interactions, including those in the distorted U-shaped region, deserve close attention.^{9b,17b}

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